Electrodeposited Polythiophene Films Provide Reproducible Samples for Laser Desorption Ion Trap Mass Spectrometry Studies

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Electrodeposited polythiophene films can provide consistent laser desorption signal levels for over 20,000 laser shots on one position of a probe tip in an ion trap. A similar lack of signal decay was observed for multiple positions on the same film. The consistency and longevity of the ion signal resulting from laser desorption of a polythiophene film are much greater than those typically obtained from simple solution residue samples. Uniform, electrodeposited polythiophene films can provide a great reduction in the uncertainty of ion production that has previously been associated with ion trapping studies utilizing laser desorption. (J Am Soc Mass Spectrom 1997, 8, 1203–1205) © 1997 American Society for Mass Spectrometry

Experimental studies of the trapping of ions created by pulsed laser desorption sampling methods such as matrix-assisted laser desorption ionization (MALDI) have been hindered by the poor reproducibility of ion production between laser shots and between samples. Ideally, only the parameter being isolated for study should vary over the course of an experiment. It is generally not possible to eliminate the excessive shot-to-shot variation in ion production, so, to compensate for this uncertainty, the mass spectra from many laser shots must be averaged for each value of the parameter being varied. Thousands of shots may then be required to complete a parametric study of ion trapping using laser desorption. Because it is desirable to exclude all extraneous variables, it is best that the mean number of ions produced for each laser shot remain constant over the number of shots used in the experiment.

In the past, samples for pulsed laser desorption ion trapping experiments have been either quaternary alkyl ammonium salt residues or biological samples combined with a matrix (MALDI) dried on a probe tip. Neither of these sample preparation methods provides uniform surfaces. The objective of the work described herein was to develop a sampling methodology that would reduce the uncertainty in ion production inherent in laser desorption ion trapping experiments. The absolute goal was to develop a sample film of uniform surface composition and structure that, when introduced on a laser desorption probe into an ion trap, would yield long lasting, consistent signals of predictable intensity for a given set of laser and ion trap operating parameters.

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Experimental

Quadrupole Ion Trap Mass Spectrometer

For all experiments described in this article, a home-built quadrupole ion trap mass spectrometer was used. The apparatus consists of a stainless steel vacuum manifold and ion trap electrode assembly [1]. The manifold was designed to allow for laser desorption sampling from a probe inserted radially through the ring electrode.

Electronics and Timing

The radiofrequency (rf) quadrupole supply used has been described previously [2]. A Stanford Research Systems (Palo Alto, CA) model SRS DG535 digital delay generator triggered a zero-crossing detector built by the Electrical Services Shop (Chemistry Department, UBC). This device monitored the rf via an antenna, and, once enabled, detected the next positive zero-crossing of the rf voltage. A trigger was sent to the laser at a small delay relative to the period of the rf after the zero-crossing was detected. This delay was set so that the signal due to desorbed ions was maximized. After the laser fired and the desorbed ions were trapped and cooled for 5 ms, the rf was ramped and the ejected ions were detected using an ETP (Sydney, Australia) model AF138 electron multiplier held at −1800 V. The signal from the detector was then amplified with a gain of 10^7 V/A by a Keithley (Cleveland, OH) model 428 current amplifier. The amplified signal was sampled by an analog-to-digital converter (ADC) with a period of 4 μs over the duration of the rf ramp. The rf amplitude was then set to zero to clear the trap, and the cycle was repeated. For all the experiments, a bath gas of He held

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at 0.8 mtorr (uncorrected cold cathode gauge reading) was utilized.

Laser and Optics

A PRA Laser Inc. (London, Ontario, Canada) UV-12 nitrogen laser was used for all the experiments. The pulsed energy output at 337 nm was ~1.5 mJ over 10 ns. For laser desorption of polythiophene, a series of Oriel (Stratford, CT) neutral density filters was used to attenuate the laser energy to ~100 μJ that was focused onto the probe tip using a 30.00 cm focal length silica plano-convex lens from Newport (Irvine, CA). The lens was positioned such that the laser was focused to a point slightly behind the probe tip that was aligned flush with the inner surface of the ring electrode. By translating the lens back, a tighter focus of the beam could be realized leading to more ion production and increased fragmentation of the desorbed species. It should be noted, however, that once a set of conditions was found that provided a strong signal level, yet did not lead to significant performance degradation through space-charge effects, the lens position was fixed for all subsequent experiments.

The irregular beam profile of the nitrogen laser rendered precise determination of the area of the beam focal spot difficult. Microscopic inspection of the surface of a polythiophene film after many thousands of laser shots showed wear on the surface in a roughly elliptical shape. The ellipse had dimensions of approximately 400 μm × 200 μm, leading to an estimated irradiance of 10^6–10^7 W/cm^2.

The lens was positioned so that the focal area of the beam was off the center of the probe tip. This enabled a fresh sample surface to be exposed to the desorption laser whenever the probe was rotated. Care was taken to prevent overlap of successive sample areas exposed to the laser beam when the probe was turned. With the beam area used here, six positions on the sample tip could be interrogated with minimal overlap between them.

Film Preparation

By using a simple two electrode cell, polythiophene was grafted as an insoluble film to the anode as a result of the oxidation of the thiophene monomer. The cell used for electrodeposition consists of a glass tube with Teflon stoppers fit into both ends. The top stopper holds the platinum tipped probe firmly in place, and can be removed to introduce the solution. The bottom stopper was press fitted to form a seal for the liquid, and houses the counter electrode, a concentric stainless steel disk. The electrode geometry was chosen so that a radially symmetric field would result when a potential was applied.

The polythiophene films used in this experiment were electrodeposited from acetonitrile solutions containing 0.25 M thiophene (Sigma, St. Louis, MO) and 0.05 M tetrabutylammonium (TBA) perchlorate (Sigma). Prior to deposition, the solutions (10 mL) were first deoxygenated for 5 min by gently bubbling nitrogen through them. During this period, the platinum tip of the probe was prepared by polishing with 5 μm grit polishing paper, followed by rinsing with methanol, then acetonitrile. Subsequent to deoxygenation, the probe was inserted into the cell and electrical connection was established between the two electrodes and the dc power supply. A stream of nitrogen was held over the solution for the duration of the electrodeposition period. All of the polythiophene data presented here came from an unrinsed film that was deposited at 3.5 V for 3 min.

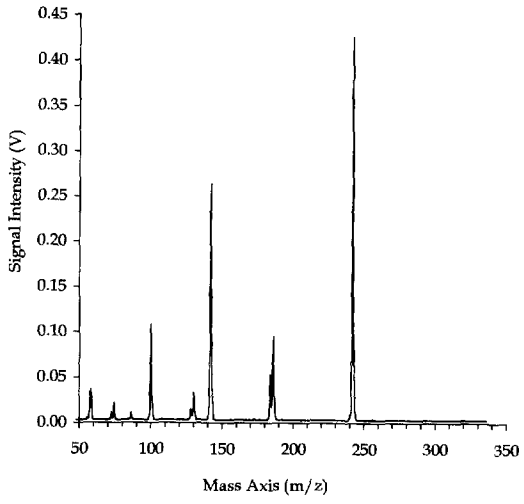

Figure 1. Mass spectrum of TBA obtained by laser desorption of a polythiophene film in an ion trap. The spectrum was obtained by integrating the spectra for 100 laser shots on the same spot on the film. The film had previously been exposed to nearly 20,000 shots at the same position.

Results and Discussion

Polythiophene films were found to yield strong ion signals from the residual electrolyte trapped within them. Figure 1 is a positive ion mass spectrum obtained by laser desorption from a polythiophene film in the ion trap. The base peak at m/z = 242 is the molecular ion for the TBA electrolyte. Other prominent peaks in the spectrum are due to fragment ions resulting from loss of alkyl groups. The source of the major peaks was established to be TBA by comparing the spectra obtained from the thiophene films with a spectrum collected from a sample prepared by directly depositing a drop of electrolyte solution onto the polished probe tip. The same peaks were observed for both the polythiophene sample and for the pure electrolyte residue sample.

The spectrum in Figure 1 was obtained by integrating the spectra from 100 consecutive laser shots. Specifically, this mass spectrum is from the final 100 of an experiment evaluating the signal decay that occurs during 20,000 laser shots on the same position of a polythiophene film. The height of the peaks relative to the noise in the baseline of the spectrum presented

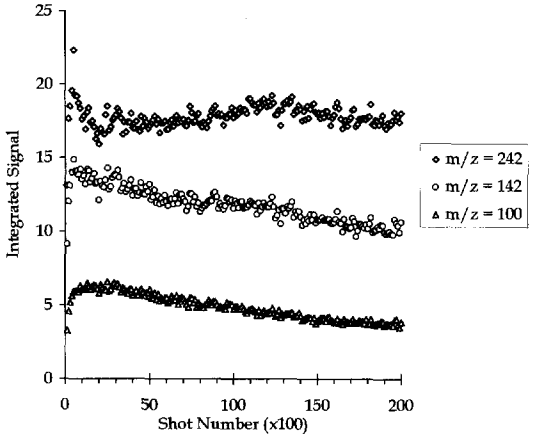

Figure 2. Decay trend in TBA ion production over 20,000 laser shots on the same position of a polythiophene film. The mean molecular ion signal level remains essentially unchanged over the period of data collection.

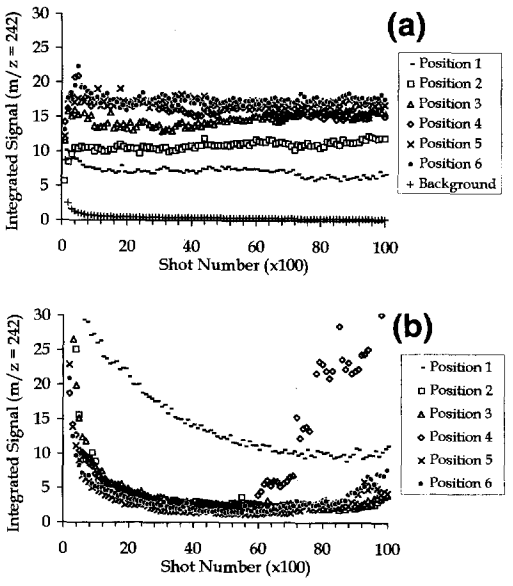

Figure 3. (**a**) Decay trend in production of TBA molecular ions by laser desorption over 10,000 shots at six discrete positions on a polythiophene film. There is no significant decay evident for any of the positions probed. (**b**) Decay trend for six positions on an inhomogeneous crystalline solution residue film. The results obtained for positions one and four are dramatically different from those of the other positions.

indicate that the ion production from the film is substantial even after 20,000 shots.

Figure 2 is a plot of the integrated peak height versus shot number at the same location on the film for the molecular ion at $m/z = 242$, and for the fragment ions at $m/z = 142$ and 100. Each point on the plot represents the average of 100 laser shots. Over 20,000 shots, the production of the molecular ion remains essentially constant, demonstrating the consistency and the duration of ion production that is possible from laser desorption at a single location on a polythiophene film.

Another desirable property that a sample film should have to render it suitable as a standard for laser desorption experiments is consistent behavior between positions on the sample. Assuming that only a finite number of ions can be produced from each position on a sample film, then, when performing experiments regarding the trapping efficiency of laser desorbed ions, it will be necessary on occasion to rotate the sample probe so that a fresh film surface can be exposed to the laser. Thus, it is expedient that there be confidence that the decay trend in ion production over a number of laser shots is the same for all positions on a sample. To test the extent to which polythiophene films can meet this requirement, the mass spectra from 10,000 laser shots on each of six discrete positions on a film were collected. Ten thousand spectra were obtained from one position, then the probe was rotated one sixth of a turn to expose a new sample surface. The decay trend for the TBA molecular ion for six positions on the film is displayed in Figure 3a. Each point represents the average integrated peak height from one hundred individual mass spectra. Over 10,000 shots, it can be seen that for each of the six positions the mean signal level remained effectively constant, although the absolute signal level varied slightly between positions. The observed deviation in absolute signal level between positions can likely be attributed to microscopic irregularities noted in the film surfaces; however, the degree of uniformity in the surface structure obtained with the conditions described above clearly suffices to provide consistent behavior.

To compare the performance of a polythiophene film to a conventional laser desorption standard sample, the same experiment was repeated with a solution residue sample. The residue sample was prepared by depositing an excess of electrolyte solution onto the probe tip. Upon drying, a crystalline film remained, but the tip was not covered uniformly. Figure 3b clearly illustrates the inconsistent ion production that resulted. Although the magnitude of the signal was initially substantial for all six positions probed, the signal levels decayed rapidly through only one thousand shots. The anomalous behavior recorded for positions one and four is characteristic of the performance normally experienced when solution residues are used as laser desorption samples. Such irregular sample surfaces are poorly suited for fundamental ion trapping studies utilizing laser desorption sampling, because the attendant uncertainty in ion production introduces an extraneous variable to the experiments.

Acknowledgments

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